Department of Environmental Quality

Copper Ion and Hypochlorite as Ballast Water Biocides

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ESG INTERNATIONAL

Michigan's Ballast Water Work Group

- Management practices and biocides are the only two methods currently available to deal with this problem.
- Hypochlorite and copper ion are potentially currently available ballast water biocides.
- On-board field testing of these two biocides should be carried out as soon as possible.

Project Objectives

- Are they effective in killing a broad range of ballast-borne biota?
- Can they be safely handled?
- Are the ultimate discharge concentrations environmentally acceptable to regulatory agencies?
- Do they damage ballast tanks?
- Do they work with sediment present?
- Are they economical and readily available?
- Are there any other practical considerations regarding their use?

Project Components

Ship board

Field trial on board M.V. Federal Yukon

Toxicity Lab

Toxicity testing in simulated / controlled conditions

Corrosion Lab

Tank Coatings and corrosion testing in simulated / controlled conditions.

Ship Board Trial

Ballast Cycle Marine Ports Europe → NOBOB Voyage → Ballast Cycle Fresh Water Ports Great Lakes

Hypochlorite tested by manual dosing using Decant tanks and test barrels

Copper Ion tested by Biomatic Ion generator dosing ballast tanks and extracting to test barrels

→

Actual NOBOB Tank residuals collected to provide sediment loads

Biota concentrated to develop meaningful data

→

Live Dead Data collected Biocide levels monitored

→

Chlorine residual verified as compliant, test liquid discharged

Ballast tanks filled to establish permissible discharge dilution levels

Toxicity laboratory testing

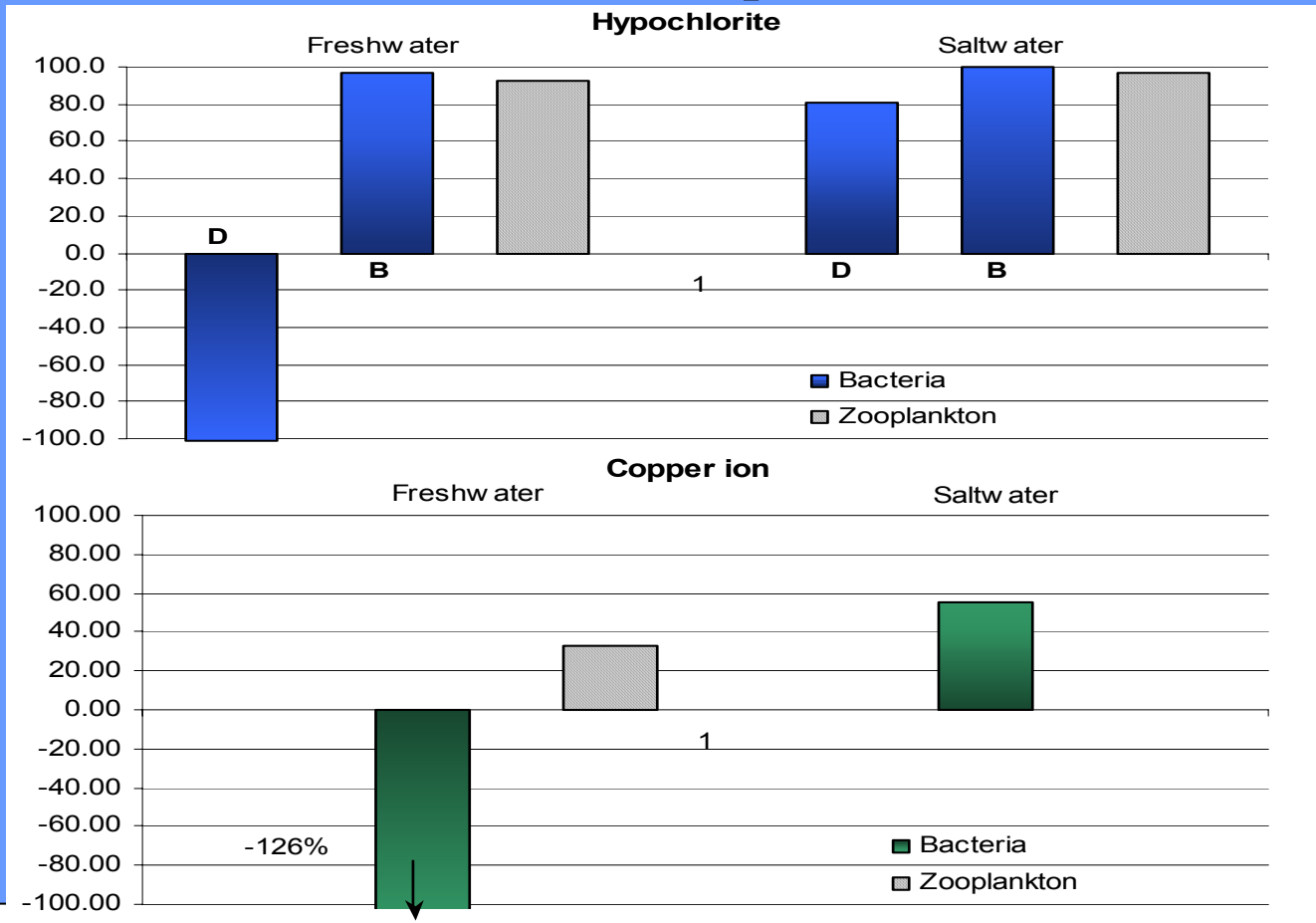
Hypochlorite and Copper ion

- Testing conducted in freshwater and saltwater
- Test conditions altered simulate ballast tank conditions (dark, cool) during a short voyage (48 hours)
- Tests conducted on fish, invertebrates (benthic and pelagic, resting stages) algae, and bacteria

Corrosion Laboratory testing

Coatings	Condition	Environment	Biocide	Medium
4 Systems Zinc Pre-weld primer Epoxy & modified Epoxy	Bare Metal	Humid (suspended above water surface)	2 Hypochlorite levels	Fresh Water
	Coated intact	Submerged constantly	2 Copper levels (separate)	
	Coated & Scribed	Splash zone (mounted on wheel)		Salt Water
		Buried (in inert sand)	Controls	

Results - Ship board



Results - Toxicity Lab

Hypochlorite toxicity to selected organisms in the laboratory (48 hr LC99)

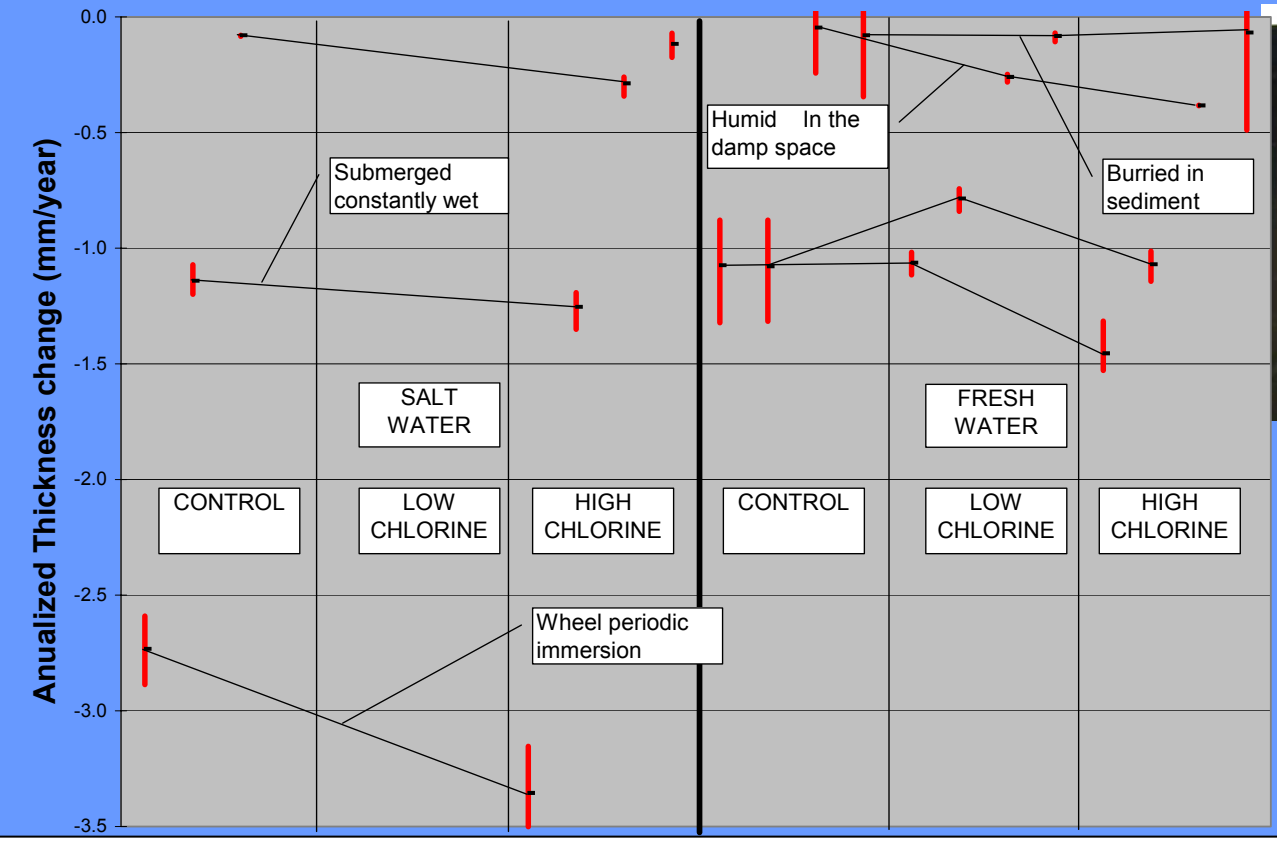
Lethal Concentration Range (ppm)	Freshwater	Marine
< 1	Alga *S. capricornutum* Alga *Nanochloris sp.* Alga *S. obliquus* Invertebrate *D. magna* (neonate)	Bacteria *V. fischeri* Alga *S. costatum*
1 to 10	Bacteria *Bacillus subtilis* Mollusc *D. polymorpha* Benthic invertebrate *L. variegates* Fish *C. carpio*	Amphipod *E. estuarius* Fish *C. variegatus*
10 to 100	Invertebrate *D. magna* – (ephippia)	
100 to 1000		Invertebrate *A.salina* (cyst)

Results - Toxicity Lab

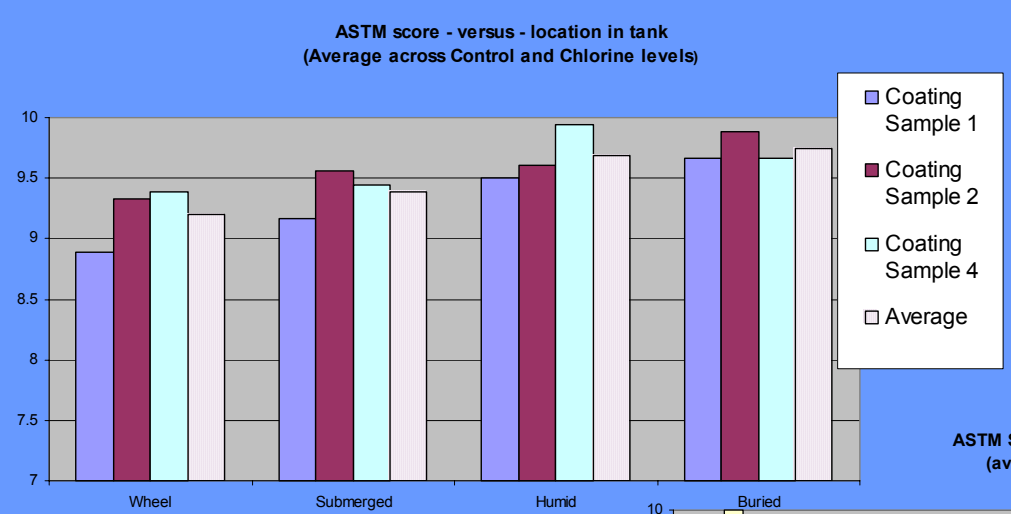
Copper ion toxicity to selected organisms in the laboratory (48 hr LC99)

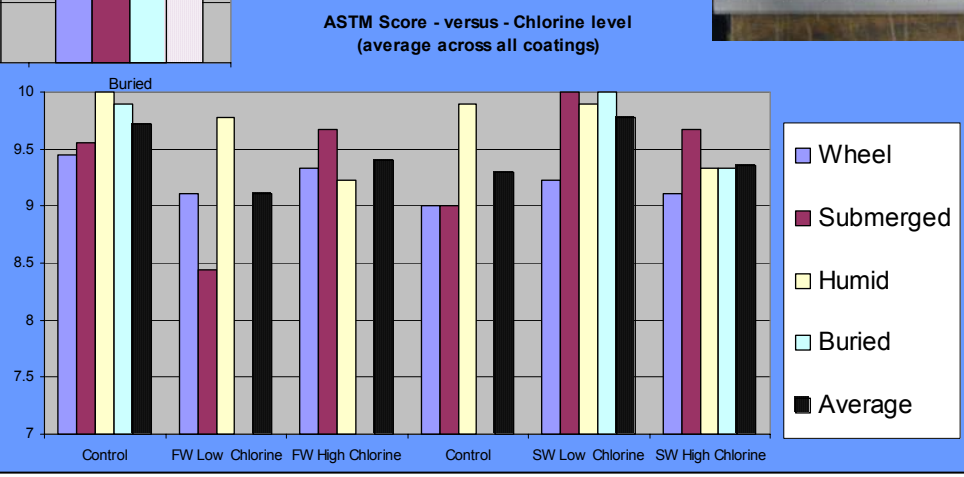
Lethal Concentration Range (mg/L)	Freshwater	Marine
< 0.2	Invertebrate *D. magna* (neonate) Alga *S. capricornutum* Alga *Nanochloris sp.*	
0.2 to 2.0	Alga *S. obliquus* Fish *C. carpio*	Bacteria *V. fischeri*
2.0 to 20	Mollusc *D. polymorpha* Benthic invertebrate *L. variegatus*	Alga *S. costatum*
20 – 200	Invertebrate *D. magna* - ephippia	Amphipod *E. estuarius* Fish (*C. variegates*)
> 1000	Bacteria *Bacillus subtilis*	Invertebrate *A.salina* (cyst)

Results - Corrosion Hypochlorite

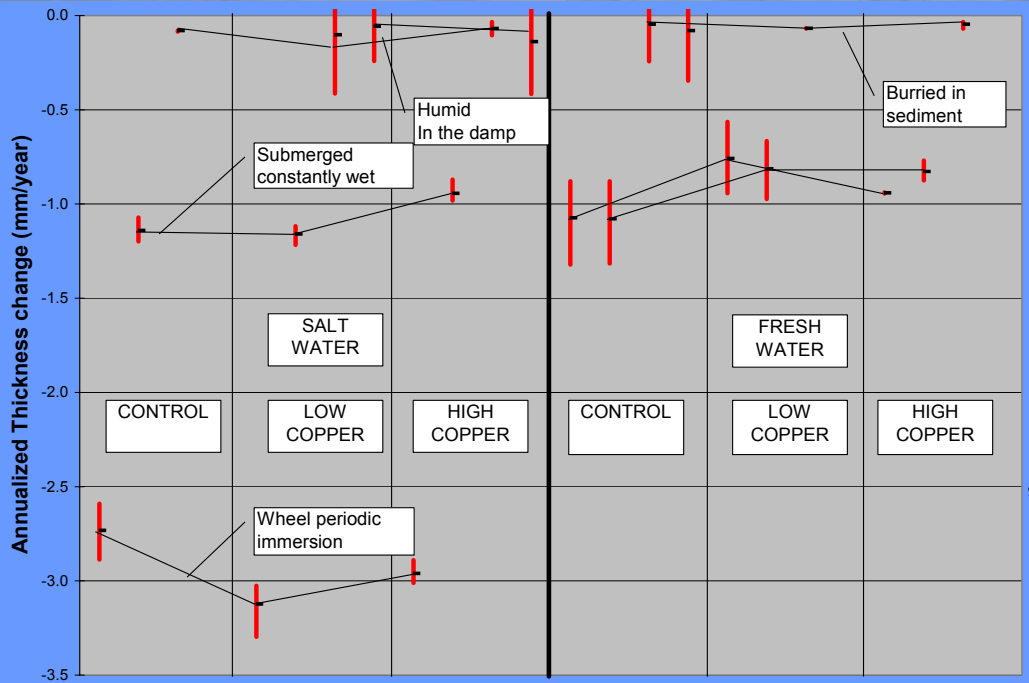


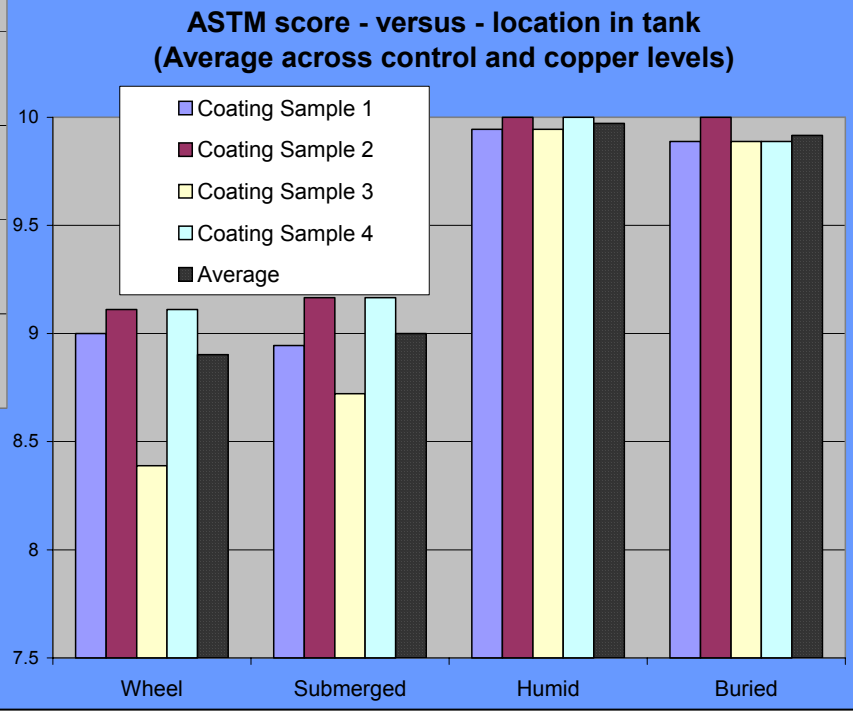
Results - Coating Hypochlorite





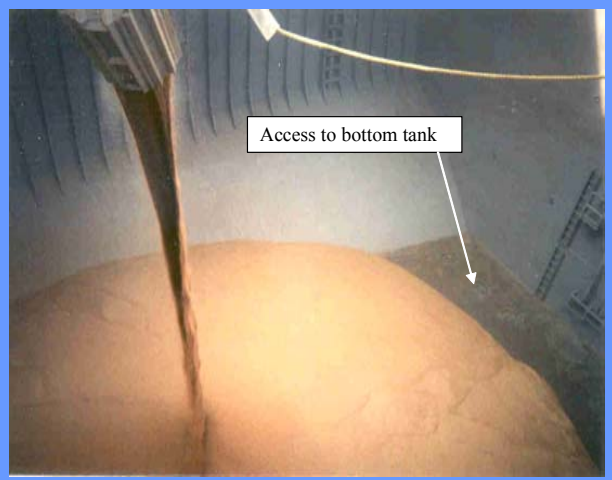
Results - Copper

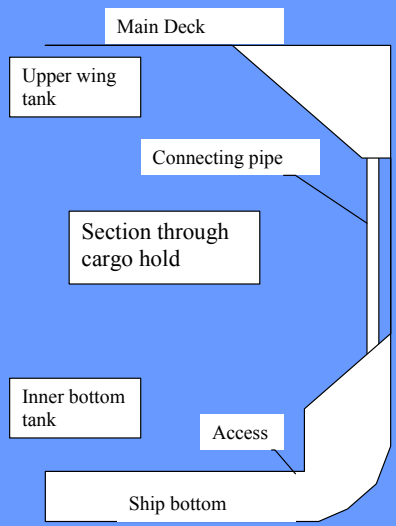


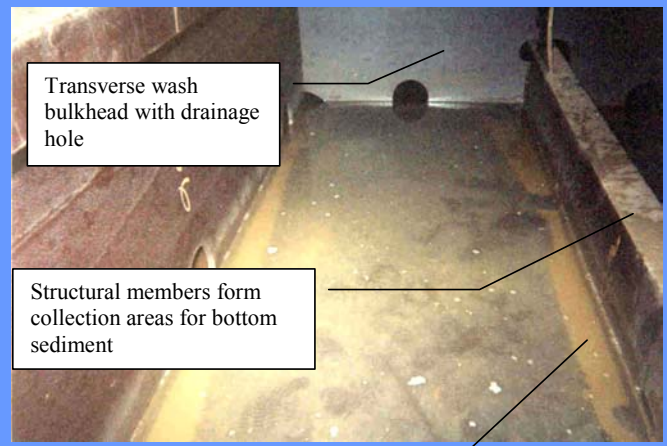


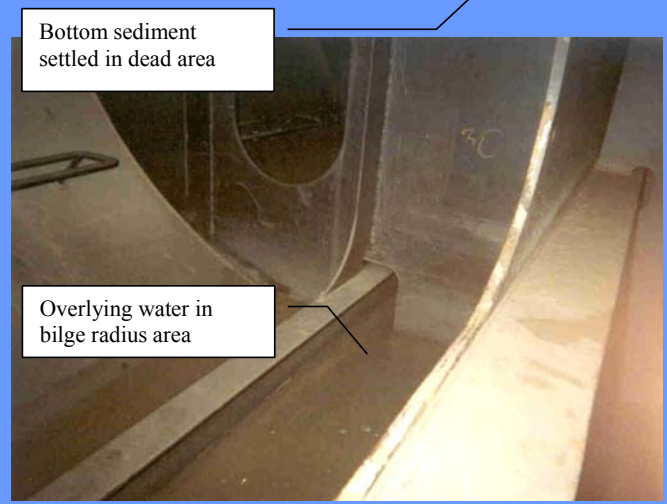
Ship tanks


Decant tanks on Deck


Access to bottom tank


Main Deck
Upper wing tank
Connecting pipe
Section through cargo hold
Inner bottom tank
Access
Ship bottom


Transverse wash bulkhead with drainage hole
Structural members form collection areas for bottom sediment


Bottom sediment settled in dead area
Overlying water in bilge radius area

Fitting Copper Generator

Impact on Shipping

	Copper Ion Generator	On Board Chlorine Generation	Purchase commercial concentration Sodium Hypochlorite	
Item	0.2 ppm on 50 tonnes	330 kg (725lbs) per day 0.8%	Buy and store onboard	Deliver to the ship as required
Capital cost	$104,696	$ 437,710	$ 207,025	$ 77,318
Element replacement cost	$18,750	$ 50,000	$ 10,000	$10,000
Element replacement frequency (years)	5	5	5	5
Ballast operations per year	12	12	12	12
Raw material costs	$ 0.09	$318	$ 504	$ 756
Vessel charter rate (per day)	$9,000	$9,000	$9,000	$9,000
Return rate	15%	15%	15%	15%
Inflation rate	3%	3%	3%	3%
Amortization period	20	15	15	15
Increase charter to maintain return	$ 48.08	$ 207.73	$104.03	$ 60.54
%increase to cost of shipping	0.53%	2.31%	1.16%	0.67%

Summary of Findings - Efficacy

Ship board studies demonstrated that in both fresh and sea water;

Hypochlorite is very effective (>90%) in reducing bacteria levels and killing many zooplankton taken in with ballast water at concentrations of ~10 mg/l (as TRC).

A copper ion generator dosing at 0.2 mg/l is of limited effectiveness in killing organisms taken in with water ballast (33% of zooplankton were killed, and bacteria were essentially unaffected).

Lab studies demonstrated that in both fresh and sea water;

Hypochlorite is very effective (>99%) in killing most organism types at a concentration of 10 mg/l.

Exceptions are resting stages such as eggs and cysts, which required much higher doses of hypochlorite for comparable kill

Copper is very effective (>99%) in killing most organism types at a concentration of 20 mg/l (as total copper).

Higher doses of copper ion were not effective at killing resting stages such as eggs and cysts.

Both hypochlorite and copper ion are hindered in their biocidal action by sediments in ballast water.

It is critical to minimize sediment in ballast water (Best Management Practices).

Summary of Findings - Operational

Copper ion biocide can

be safely handled,

is relatively low cost, and

requires no special training or safety precautions on-board ship.

Copper Ion generation on board is always available.

There are no quantifiable, detrimental effects of copper on the structural integrity of the ship.

Copper discharge rates are unlikely to meet environmental regulatory standards if applied at effective dosages.

Hypochlorite can be safely handled, provided that;

proper accommodations and procedures are in place for both the hypochlorite and the neutralizing agent (sodium bisulfite).

Depending on the concentration / volume stored and or carried, this includes;

Storage tanks, piping, pumps, metering, monitoring and control, crew training, safety procedures.

Bulk hypochlorite is readily available at ports or may be generated on board from common salt.

Over a typical life time exposure to hypochlorite at a concentration of 10 mg/l TRC, ballast tank coating degradation and corrosion is not significantly increased. Corrosion becomes more significant at higher levels of hypochlorite.

Hypochlorite discharge levels can be achieved by addition of neutralizing agent. By products are acceptable to regulators.

Way Ahead

In order to answer questions about the efficacy and practicality of hypochlorite and copper ion with sediment and plankton present, further testing should be done in actual ballast tanks and various harbor water quality situations.

The total dosage necessary to achieve an effective kill increases for both biocides in ballast water containing high amounts of sediment and the minimum level is indeterminate. Studies are needed to determine the magnitude of this effect due to both suspended sediment entering with ballast water, and settled sediment in the ballast tanks.

Costs, efficacy, regulatory acceptability, and practicality can all be affected by sediments

Sediment can minimized through Best Management Practices, this needs to be quantified.